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Towards reliable conformational energies: hexane conformers

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The fact that both many small molecules and in particular macromolecules can adopt a variety of different conformations is of eminent relevance with respect to their properties. The precise geometry and the relative energies of different conformations of small molecules have been the issue of many studies in the past. Small molecules can usually be studied in the gas-phase, and their structure can be experimentally resolved in great detail [1]. Quite some problems still remain to be solved, however, in particular when no direct experimental access is available. It is in those cases that first-principles or ab-initio type calculations can be of great value. In addition, ab initio based information has an important additional value in the development of empirical potentials, e.g. force fields, for large molecules like (bio)polymers, which are generally based on potential energy surfaces of similar, monomer-like, fragments.

The alkanes belong to a class of very simple molecules, while a polymeric form, polyethylene, is the simplest polymer. The all-trans conformation is the energetically most stable form. However, in the liquid state and in the amorphous polymer the fraction of gauche bonds increases (of the order of 40% at ambient temperature). Experimentally, a single isolated gauche bond is about 0.5 kcal/mol [1,2] less stable than the trans bond. Whereas the relative energy of a chain with gauche bonds increases with the fraction of gauche bonds, this increase is not purely additive in the number of gauche bonds, particularly not when the gauche bonds are neighbours or next-nearest neighbours in the alkane or polyethylene chain.

It appears generally accepted that the energy of a conformer becomes less favourable with increasing gauche content. However, in a theoretical study Frey et al. [3] reported the surprising result that the ggg conformer in hexane is more stable than the gtg conformer. Although somewhat counterintuitive, this result has been extracted from the highest level of ab initio calculations reported on hexane until 1999.

In order to investigate the somewhat unexpected result reported by Frey et al. in mre detail, we have applied Hartree-Fock and post-HF methods to evaluate the relative stability of these conformers. We find 4 that at levels higher than MP2 the gtg conformer is found more stable than the ggg conformer, in agreement with the conventional idea that each additional gauche bond causes a further decrease in stability of the conformer. DFT methods were also applied, but although DFT methods including gradient corrections show correct qualitative behaviour, quantitatively the relative energies are far off compared to the post-HF results.

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